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MINERALOGICAL INVESTIGATION OF TEXASGULF ZINC PLANT RESIDUES

by

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SUMMARY

A mineralogical investigation was performed on three different zinc plant residues from the Kidd Creek operations of Texasgulf Canada Ltd. (now Kidd Creek Mines Ltd.). Samples of a neutral leach residue and a high-acid leach residue were almost identical morphologically but somewhat different compositionally. A jarosite precipitation residue was radically different from the first two residues both morphologically and compositionally.

The phases in the neutral leach residue occur largely as fine-grained particles bound in aggregates up to several hundred micrometres in size and as individual grains and small clumps. The binder in the aggregates is an iron-rich, compositionally complex, gel-like substance. Principal phases in the residue include zinc ferrite (ZnFe_2O_4) and jarosite; silicates, oxides, hydroxides and sulphates account for most of the remainder.

The high-acid leach residue differs from that of the natural leach residue in that it contains appreciably more gypsum and traces of silver-bearing phases. The gel-like binder is richer, on average, in its silica content.

The jarosite precipitation residue comprises separate grains, is more uniform in size and lacks the gel-like binder of the neutral, and high-acid leach residues. In addition, fewer phases are present and these are dominated by natrojarosite with smaller amounts of zinc ferrite.

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INTRODUCTION

Three samples of Texasgulf zinc-plant residues were received from L.A. Ryan in September 1981. Mr. Ryan requested that the residues be subjected to mineralogical analysis. It was agreed prior to the receipt of the samples, that the work be done in the Mineralogy Section, Mineral Processing Laboratory, CANMET, on a full cost-recovery basis (Job No. 025109).

SAMPLES

Each of the three residues consisted of several hundred grams of wet, fine-grained powder and were labelled "Neutral Leach Residue", "High-Acid Leach Residue" and "Jarosite Precipitation Residue". Mr. Ryan stated, in an accompanying letter that the residues were the result of hydrometallurgical tests on roaster precipitator dust, a sample of which had been studied in this laboratory in February 1981⁽¹⁾. The letter also included partial analyses of the residues (Table 1), as well as a list of the expected components of each residue (Table 2).

Table 1 - Partial chemical analyses of the residues*

Residue	weight per cent					g/tonne
	Zn	Fe	Pb	SiO ₂	Sn	(ppm)
Neutral leach residue	21.58	27.9	1.24	5.32	0.54	330
High-acid leach residue	7.82	16.5	4.84	24.5	1.59	1,160
Jarosite precipitation residue	5.48	31.7	0.24	1.90	0.20	98

* Analyses supplied by L.A. Ryan, T.G.S.

Table 2 - Expected components of the residues*

Residue	Expected components
Neutral leach residue	$\text{Fe}(\text{OH})_3$, ZnFe_2O_4 , SnO_2 , SiO_2 , PbSO_4 or jarosite, Ag**
High-acid leach residue	ZnFe_2O_4 , Pb jarosite, SiO_2 , SnO_2 , Ag**
Jarosite precipitation residue	Na jarosite, ZnFe_2O_4 , SiO_2 , SnO_2 , Pb jarosite, Ag**

* Information supplied by L.A. Ryan, T.G.S.

** Ag form undetermined.

METHOD OF INVESTIGATION

The residues were dried in air. A representative portion of each residue was extracted and submitted for X-ray diffraction analysis (diffractometer and Debye-Scherrer) in order to identify the crystalline phases present and to assess their relative quantities. Other portions were mounted in polished sections and studied using the combined methods of optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis and energy dispersive analysis (EDX).

RESULTS

An examination of the partial metal contents of the residues (Table 1) showed that if a value of unity is assigned to the weight percentages for Pb, Si, Sn and Ag in the neutral leach residue, their relative proportions in the other two residues are almost constant (Table 3). The proportions of Fe and Zn do not follow this pattern.

Table 3 - Calculated ratios for Pb, Si, Sn and Ag in the residues

Residue	Element ratios			
	Pb	Si	Sn	Ag
Neutral leach residue	1.0	1.0	1.0	1.0
High-acid leach residue	3.9	4.6	2.9	3.5
Jarosite precipitation residue	0.2	0.4	0.4	0.3

The results of X-ray diffraction analysis of the residues are summarized in Table 4. It should be borne in mind that only crystalline phases can be detected by X-ray diffraction. In addition, differences exist in the degree with which minerals diffract X-rays. For example, quartz diffracts X-rays very efficiently and as little as 1 to 2 per cent can readily be detected in a sample; minerals such as a jarosite or feldspar diffract X-rays poorly and may require as much as 10 to 20 per cent to be detected by this method. Oxides can usually be detected in amounts of 5 per cent or larger. $\text{Fe}(\text{OH})_3$ was not detected in the neutral leach residue.

Table 4 - X-ray diffraction analysis of the residues*

Residue	Phases identified*		
	Major	Minor	Trace
Neutral leach residue	zinc ferrite	jarosite	quartz
High-acid leach residue	zinc ferrite	jarosite gypsum	quartz
Jarosite precipitation residue	zinc ferrite natrojarosite	-	-

* Analyses of the residues by E.J. Murray.

** The phases identified and their estimated proportions reflect their efficiency in diffracting X-rays and may not be truly representative of the amounts present.

Physical Characteristics of the Residues

Studies by optical microscopy, scanning electron microscopy and electron microprobe have shown that the neutral leach residue and high-acid leach residue are extremely fine-grained and compositionally complex. The majority of the particles in these residues are less than 20 micrometres in size* and many are smaller than one micrometre. Exceptions include some of the grains of quartz, zinc ferrite and gypsum which are as large as 70, 50 and approximately 250 micrometres, respectively. The examination of these two residues was complicated by the presence of a gel-like substance which has a variable composition and is probably amorphous to X-rays. Although many of the grains in the residues occur as separate individuals, the gel has formed as a binder which has cemented a majority of the grains into aggregates (Figures 1 and 2). This gel may be a result of the leaching procedures abetted by the fact that the samples of the residues were received still wet (in bottles) and were allowed to dry in air before being mounted in polished section. Shrinkage cracks are visible in some areas of the gel (in polished section) which suggests that the residues may not have been completely dry when mounted.

The jarosite precipitation residue differs from the other two residues in that the grains are present as separate individuals. Grain size is more uniform and there is no evidence of a gel (Figure 3).

Chemical Composition of the Residues

The chemical composition of the residues and their constituent phases is variable. EDX analysis with the SEM showed that in addition to the major elements (Fe, Zn and Si) and minor elements (Sn, Pb and Ag) reported by L.A. Ryan (Table 1), these residues also contain significant to trace amounts of Na, S, Ca, Al, Ba, Mn, K, Cu, Cl, Ti, P, Ce, La, In, Se, and Sb. However, not all of these additional elements were found in all three residues.

* The term "size" as used in this report refers to the greatest dimension of the mineral grains or phases observed in polished section.

Mineralogy of the Residues

(a) Neutral leach residue

The neutral leach residue was reported to contain $\text{Fe}(\text{OH})_3$, zinc ferrite, SiO_2 , SnO_2 and lead sulphate or lead jarosite (Table 2). X-ray diffraction analyses confirmed the presence of zinc ferrite (ZnFe_2O_4), a jarosite and quartz (Table 4). $\text{Fe}(\text{OH})_3$ was not detected but may be amorphous to X-rays.

This residue is extremely fine-grained and, although some zinc ferrite and quartz are as large as 70 micrometres most grains are smaller than 10 to 20 micrometres in size (Figures 1 and 4). The major portion of these grains occur within the aggregates (Figure 1) and are usually bound together by a gel-like substance. The gel is iron-rich, compositionally variable and complex. It decomposes quite readily under the electron beam of the microprobe. A smaller quantity of grains occur as separate particles and tiny aggregates.

Microscopical studies on the polished sections of the neutral leach residue (approx. 1000X) have shown the presence of numerous minute grains (from <1 to $3 \mu\text{m}$) of what is probably the jarosite. These particles occur largely as inclusions within the gel binder of the larger aggregates and to a lesser extent as separate grains and small aggregates. The identification of these particles as jarosite could not be confirmed by either powder X-ray diffraction studies or by quantitative electron microprobe analysis because of their minute grain size. However, the identification of these grains as a jarosite is probably correct, because the presence of significant amounts of jarosite has already been confirmed by diffractometer analysis of the residue (Table 4) and the optical properties of these grains are similar to those of jarosite. EDX studies from several small aggregates of jarosite(?) and from areas of the gel-like binder (Figure 5) have shown them to have some compositional similarities. The composition of the binder, although variable from spot to spot is largely $\text{Fe} > \text{Zn} > \text{S} > \text{Si} > \text{Al}$, Cu, Mn $\pm$ Pb, Cl, and that of the jarosite is $\text{Fe} > \text{Zn} > \text{S} > \text{Si} > \text{Al} > \text{Cu}$.

Minor phases identified in the neutral leach residue are barium sulphate (barite), feldspar, SnO_2 (cassiterite), oxides or hydroxides of manganese and/or iron, gypsum, incompletely reacted sphalerite and a calcium alumino-silicate.

EDX studies also showed that the zinc ferrite grains usually contain trace amounts of copper and occasional traces of sulphur. In addition, small amounts of potassium and trace amounts of Pb, Cu, Zn, Si and Al were detected in some of the hydroxides (Mn/Fe).

(b) High-acid leach residue

The high-acid leach residue exhibits the same morphology in polished sections as the neutral leach residue. The major portion of the grains occur in aggregates (Figure 2), often bound together by a gel-like substance (Figures 6, 7 and 10) whose composition is similar to, but somewhat more complex, than that of the gel-like substance in the neutral leach residue.

The major phases in this residue are zinc ferrite and jarosite(s). Other phases identified include small amounts of gypsum* and quartz, minor to trace amounts of barium sulphate (barite), feldspar, SnO_2 (cassiterite), iron oxide, residual sphalerite, $\text{Ag}_2\text{S}(\text{?})$ as well as chalcopyrite and single grains of ilmenite, a rare earth phosphate of Ce/La and a silver-bearing antimony sulphosalt. These phases are generally very fine-grained with the majority much smaller than 20 micrometres in size. The larger grains tend to be zinc ferrite, quartz and gypsum with maximum dimensions of 80, 100 and 250 micrometres, respectively. The residue contains numerous minute particles similar in size, occurrence and composition to the jarosite(?) of the neutral leach residue. They are present largely as inclusions in the gel of the aggregates (Figure 7) and as separate grains and smaller aggregates. X-ray diffractometer analysis has already confirmed the presence of significant amounts of jarosite in this residue (Table 4). The confirmation of the identity of these minute particles as jarosite was enhanced by using the non-dispersive, wavelength spectrometry system of the electron microprobe, which indicated that these grains are sulphates**. This test was performed on the

* Identity of gypsum confirmed by powder X-ray diffraction analysis.

** The discrimination between sulphur in a phase as either sulphide or sulphate is based on a shift in the wavelength of the $\text{SK}\alpha$ X-ray emission line which is a result of differences in chemical bonding. This shift can be detected using the method of non-dispersive wavelength spectrometry.

grains in several small aggregates whose optical characteristics are those of a jarosite. Qualitative analyses on several jarosite clusters using the EDX system of the SEM showed that the jarosite consists of $\text{Fe} \gg \text{Zn} \gg \text{Si} \gg \text{Al}$, Cu and Mn. Similar studies on the zinc ferrite showed its composition to be the same as that in the neutral leach residue.

Several grains of silver-bearing phases were found in this residue: five grains of $\text{Ag}_2\text{S}(?)$; one grain of a silver-bearing antimony sulphosalt; and a silver-bearing area of the gel (Figure 10). The grains of $\text{Ag}_2\text{S}(?)$ (<1 to $4 \mu\text{m}$ in size) occur within the complex aggregates. The largest grain ($4 \mu\text{m}$) was used to confirm that this phase is a sulphide** and not a sulphate such as Ag_2SO_4 . The other grains were too small for this test as the electron beam of the microprobe overlapped onto the surrounding medium, where sulphates are present, and prevented this discrimination. However, it is reasonable to assume that these grains are also sulphides. The EDX studies of these grains also showed that two of the smallest grains contain small amounts of chlorine. The occurrence of the silver-bearing sulphosalt (PbSbS) consisted of a single grain, 2 micrometres in diameter, lodged in an aggregate. Its silver content could not be measured quantitatively because of its minute size, but it is certainly more than a trace amount. An unusual silver occurrence was located in a small area of the gel (Figure 10) during EDX studies of the aggregates. The silver is a significant element (Figure 11) in the silica-rich area of the gel (Figure 12). Other elements occurring in this immediate area are typical of those found in other areas of the gel.

The composition of the gel in this residue is quite similar to that of the gel in the neutral leach residue, except that its average silica content is appreciably higher. This probably accounts for the high silica content of this residue (Table 1). Qualitative analyses from numerous areas of the gel using the EDX system of the SEM have shown that the gel, although variable in composition, consists of $\text{Fe} \gg \text{Zn}, \text{Si} \gg \text{Al} \pm \text{Ca}$, K, Pb $>$ Cl, Ba and In. Detection of the minor elements was irregular. It was also found that

** See footnote on page 6.

a few limited areas of the gel contain lead in sufficient concentration to be displayed by X-ray mapping with the SEM (Figures 8 and 9). Whether these areas represent a lead jarosite, lead sulphate (PbSO_4) or simply a concentration of lead in the amorphous gel could not be established.

(c) Jarosite precipitation residue

This residue consists largely of jarosite (Figure 3). Smaller amounts of zinc ferrite and some quartz together with minute amounts of SnO_2 , manganese hydroxide*** or oxide, iron hydroxide or oxide and incompletely reacted sphalerite account for the remainder.

Unlike the other residues there is neither a gel-like substance nor any aggregates in the jarosite precipitation residue. The jarosite and other phases are present almost entirely as separate particles with the former exhibiting a very uniform grain size. Most of the jarosite is between 2 and 15 micrometres in size although several grains up to 35 micrometres were observed. The other phases are coarser grained, with quartz and zinc ferrite up to 75 μm . Quantitative electron microprobe analyses were made on several of the largest jarosite grains. The results showed them to be a natrojarosite containing small and variable amounts of lead or potassium substituting for sodium, and aluminium in substitution for iron (Table 5). This is the only occurrence of lead found in the residue. Based on the microprobe analysis of the natrojarosite and its estimated abundance in the residue, the lead content of the natrojarosite (0.60 wt % Pb) is sufficient to account for most, if not all of the reported lead in the residue (0.24 wt % Pb). EDX studies confirmed that the composition of the zinc ferrite is the same as in the other residues.

No silver-bearing phases were found in the residue, nor was silver detected as a trace element in the natrojarosite. Even if all the reported silver in the residue (98 ppm Ag) was present in the natrojarosite in substitution for sodium, its concentration would be too low to be detected by electron microprobe analysis. The limit of detection for silver in natrojarosite by this method is approximately 250 ppm Ag.

*** X-ray diffraction analysis (Gandolfi camera) of several of these grains showed them to be amorphous to X-rays.

Table 5 - Microprobe analysis of the natrojarosite

Average composition		Range in composition
Element	wt %	wt %
Na	4.0	3.2 to 4.6
Pb	0.6	0.0 to 1.1
K	0.1	0.1 to 0.2
Fe	32.3	29.9 to 33.1
Al	1.1	0.5 to 2.2
S	<u>13.2</u>	constant
	51.3	

CONCLUSIONS

The mineralogical investigation of the neutral leach residue, high-acid leach residue and jarosite precipitation residue permits the following conclusions to be made:

1. Tin was identified in the three residues only as cassiterite (SnO_2) and has apparently remained unaffected in its passage through the metallurgical procedures.
2. The occurrence of silver in the residues could only be assessed in the high-acid leach residue. The Ag_2S grains are minute, enclosed in the Fe-Zn-Si gel and may have been unaffected.
3. The silica in the neutral and high-acid leach residues is present largely as a component of the gels and as quartz. Minor to trace amounts also occur as feldspar and other silicates and as a trace impurity in jarosite. The large increase in the silica content of the high-acid leach residue relative to that of the neutral leach residue is due in large part to the increased silica content of the gel. Silica was found only as quartz in the jarosite precipitation residue.

4. Except for isolated and very small occurrences, lead was found only as a minor to trace element in various phases in all three residues. Because of the complexity both compositional and morphological, its presence in the neutral and high-acid residues cannot be defined. The microprobe analysis of the natrojarosite in the precipitation residue has shown that the lead occurs either as a variable and minor element substituting for sodium in this phase, or as minute, irregular and imperceptible inclusions of lead jarosite.

ACKNOWLEDGEMENTS

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REFERENCES

1. Petruk, W. "Mineralogical studies of a Texasgulf roaster precipitation dust"; Ore Processing Laboratory; Mineralogy Report M-3171; CANMET, Energy, Mines and Resources Canada; 1981.

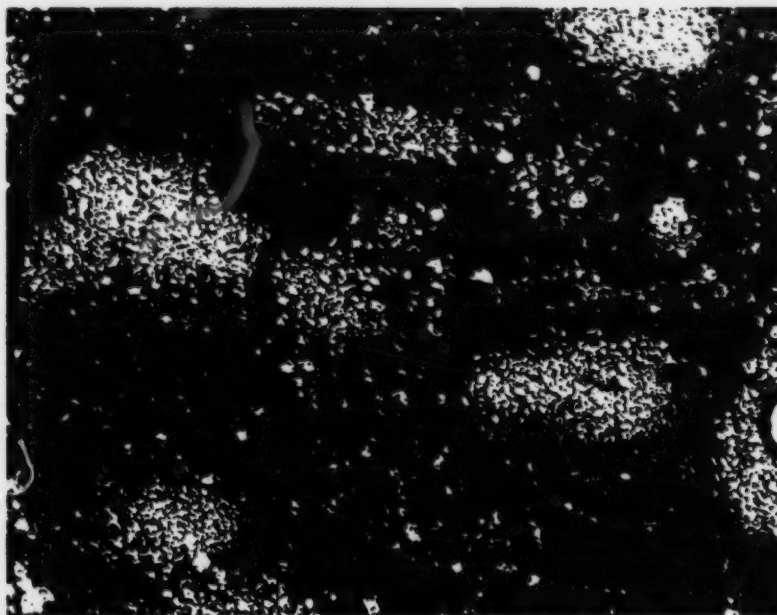


Fig. 1 - Secondary electron micrograph (65X) of the neutral leach residue showing the predominance of variable aggregates over separate grains. The black background in the micrograph is the mounting medium.

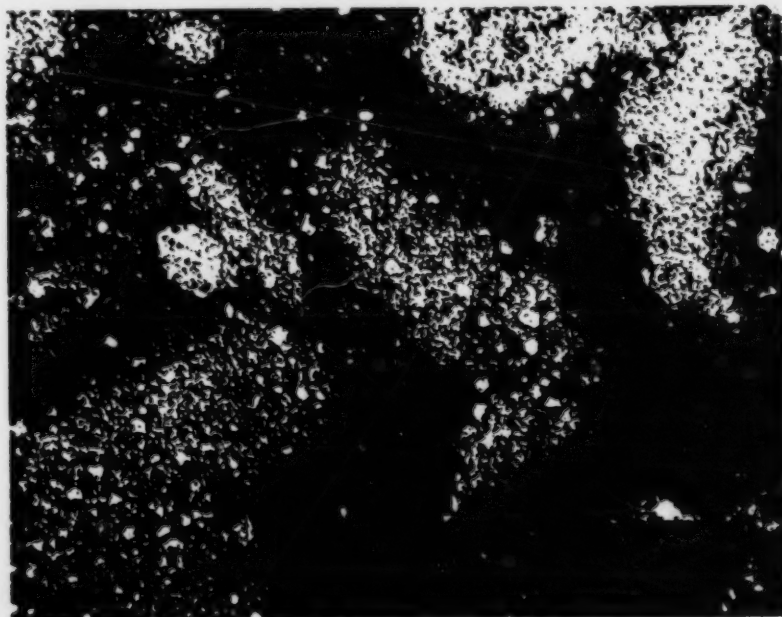


Fig. 2 - Secondary electron micrograph (65X) of the high-acid leach residue showing the same abundance of aggregates as above (Figure 1).

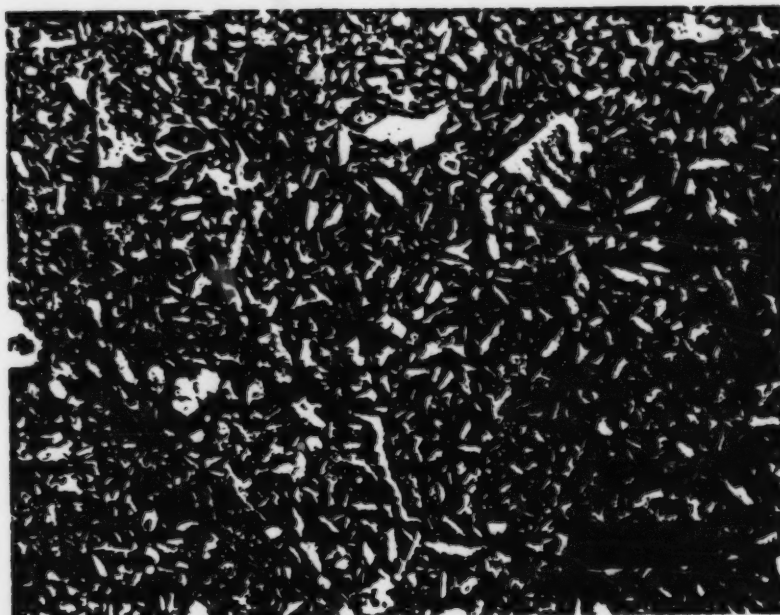


Fig. 3 - Secondary electron micrograph (620X) of the jarosite precipitation residue showing the discrete and uniform grains of jarosite (medium grey). Smaller amounts of spinel (greyish white) are also present.



Fig. 4 - Secondary electron micrograph (620X) of the neutral leach residue showing numerous grains of spinel (A), with a manganese oxide or hydroxide (B) and barite (C). The grains are bound in an aggregate by a gel-like substance (D). The black areas are mounting medium.

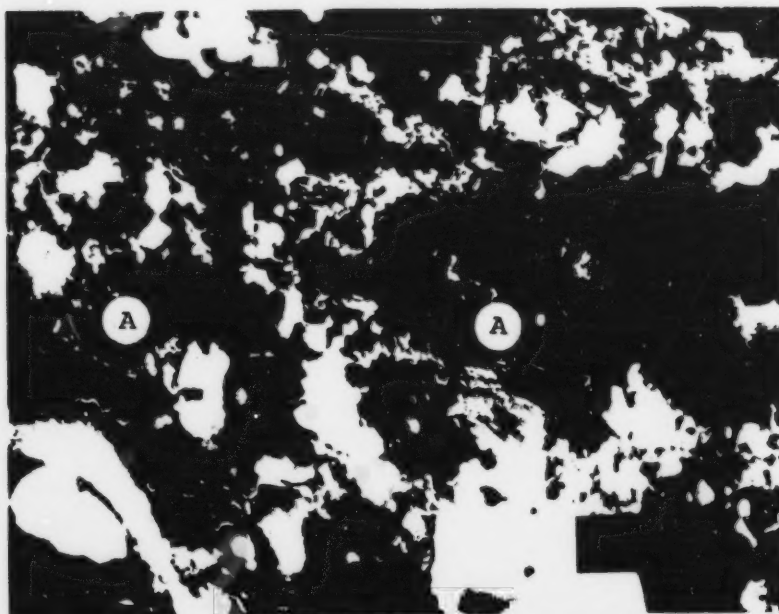


Fig. 5 - Secondary electron micrograph, at higher magnification (3200X), of area D in Figure 4 showing the gel-like binder (A) of an aggregate in the neutral leach residue. EDX studies of the gel show that the elements present, in their approximate order of abundance include Fe, Zn, S, Si, Al and Cu. The white grains are essentially spinel.

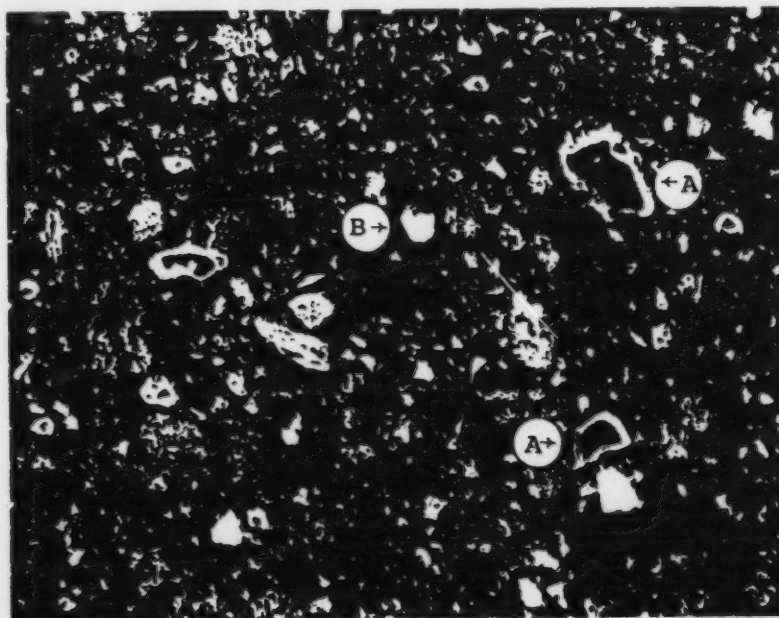


Fig. 6 - Secondary electron micrograph (300X) of the high-acid leach residue showing the typical phases and their grain size in an aggregate. Most of the smaller grains are either spinel (greyish white) or silicate (medium grey). Several larger grains of SiO_2 (A) and one of SnO_2 (B) have been marked.

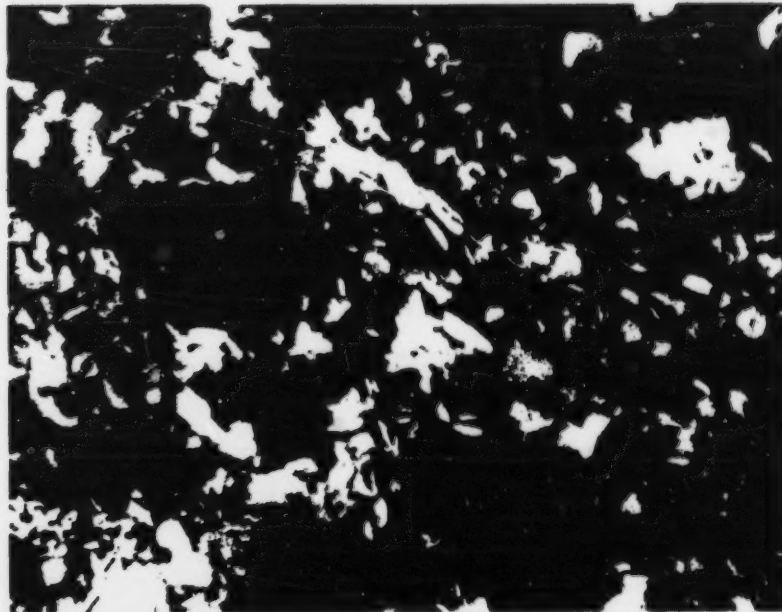


Fig. 7 - Secondary electron image of an aggregate in the high-acid leach residue at high magnification (3200X) showing the minute size of many of the grains entrapped in the gel binder. The white grains are largely spinel. EDX studies from medium grey to dark grey areas showed the following elements: Fe, Si, S, Zn, Al, Mn $\pm$ Pb, Cl, Cu, Ba and In. (Jarosite? and gel).

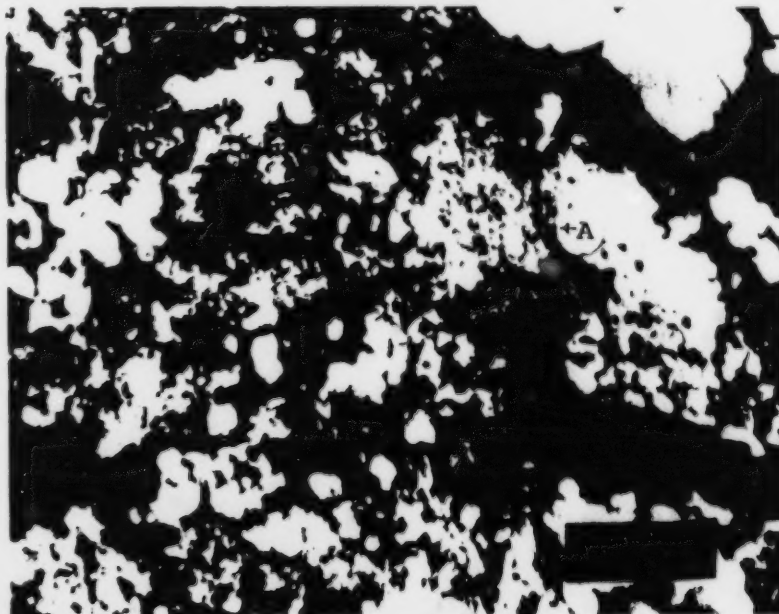


Fig. 8 - Secondary electron micrograph (3200X) of another area of an aggregate in the high-acid leach residue. The area marked (A) in the gel contains significant Pb and may be an area of Pb-jarosite (see Figure 9). Again, the white grains are mainly spinel.



Fig. 9 - X-ray micrograph for PbM_n from the identical area of the high-acid leach residue shown in Figure 8. The concentration of lead is evident (A). The other dots are normal background.

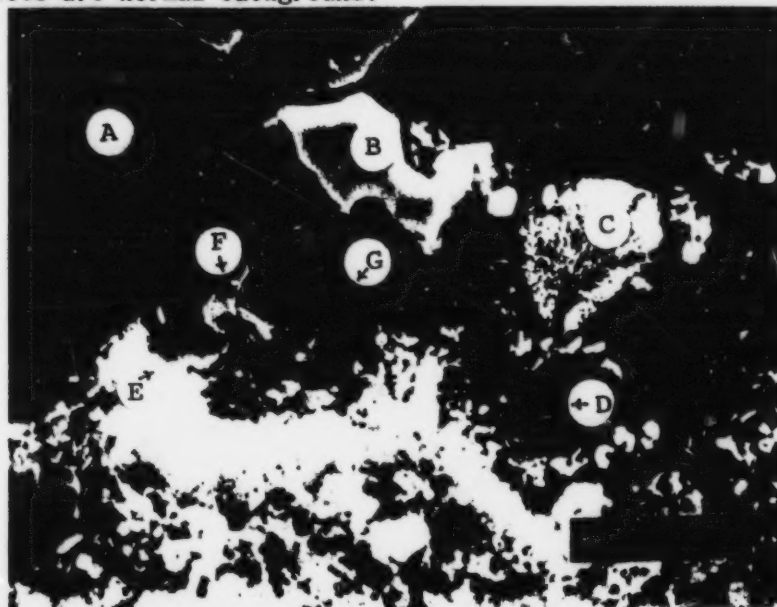


Fig. 10 - Secondary electron micrograph (1700X) of a complex area of an aggregate in the high-acid leach residue. The siliceous gel surrounding the black hole (areas E, F and G) contains some Ag; other elements present include $Si > Fe > Zn$, Al and Cl. Areas F and G also contain trace amounts of Pb, Cu, Mn and Se. The marked inclusions are spinel (B), iron oxide (C) and SiO_2 (D). The minute white inclusions are largely oxides. The mounting medium of the polished section is A.



Figure 11 - X-ray micrograph for AgLa from the identical area of the high-acid leach residue shown in Figure 10. The concentration of silver (A) about the hole is evident.



Figure 12 - X-ray micrograph for SiK_α from the identical area of the high-acid leach residue shown in Figure 10. The distribution of the silica in the gel is evident. The few areas of concentration of silica represent SiO₂.